

**EXHIBIT B**

Presentation by Dr. James C. Stevens of The Dow Chemical Company

# The Use of High Throughput Experimentation In Catalyst Research

J. C. Stevens, R. Rosen

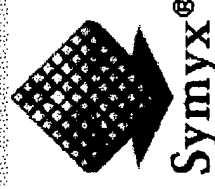
The Dow Chemical Company  
Freeport, TX

T. Boussie, G. Diamond, C. Goh, K. Hall, A. M. LaPointe, M. Leclerc,  
C. Lund, V. Murphy, J. Shoemaker, H. Turner, U. Tracht, T. Uno

Symyx Technologies  
Santa Clara, CA

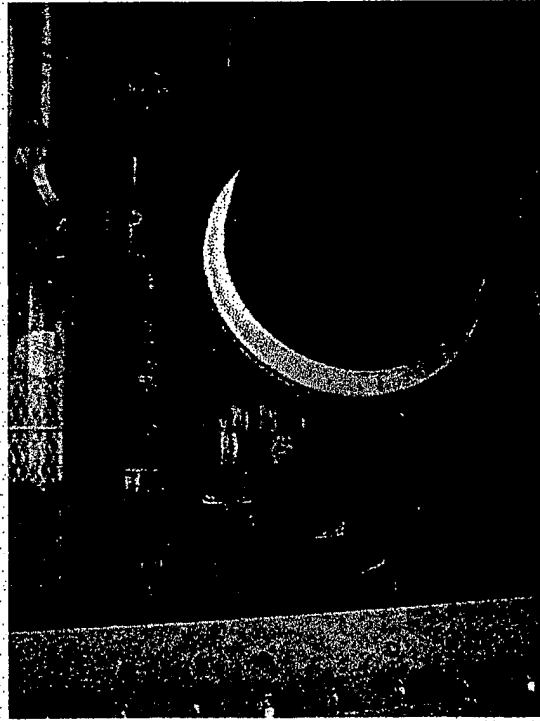


FLEXPO 2002

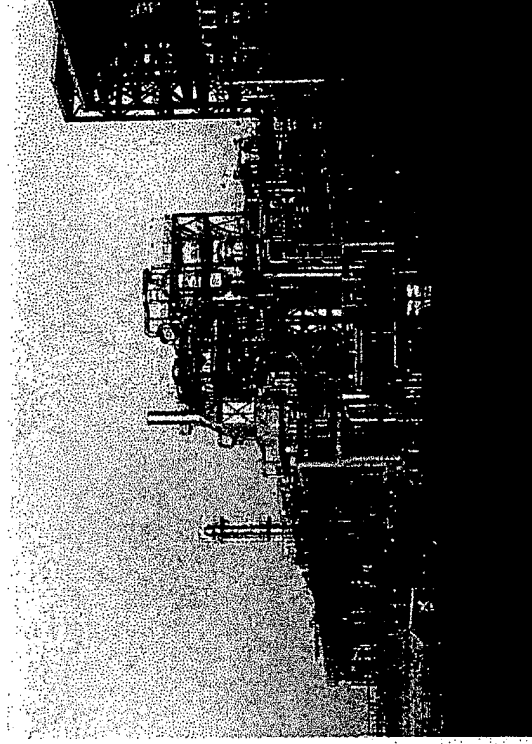


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# New Polyolefin Catalysts Drive New Business Growth

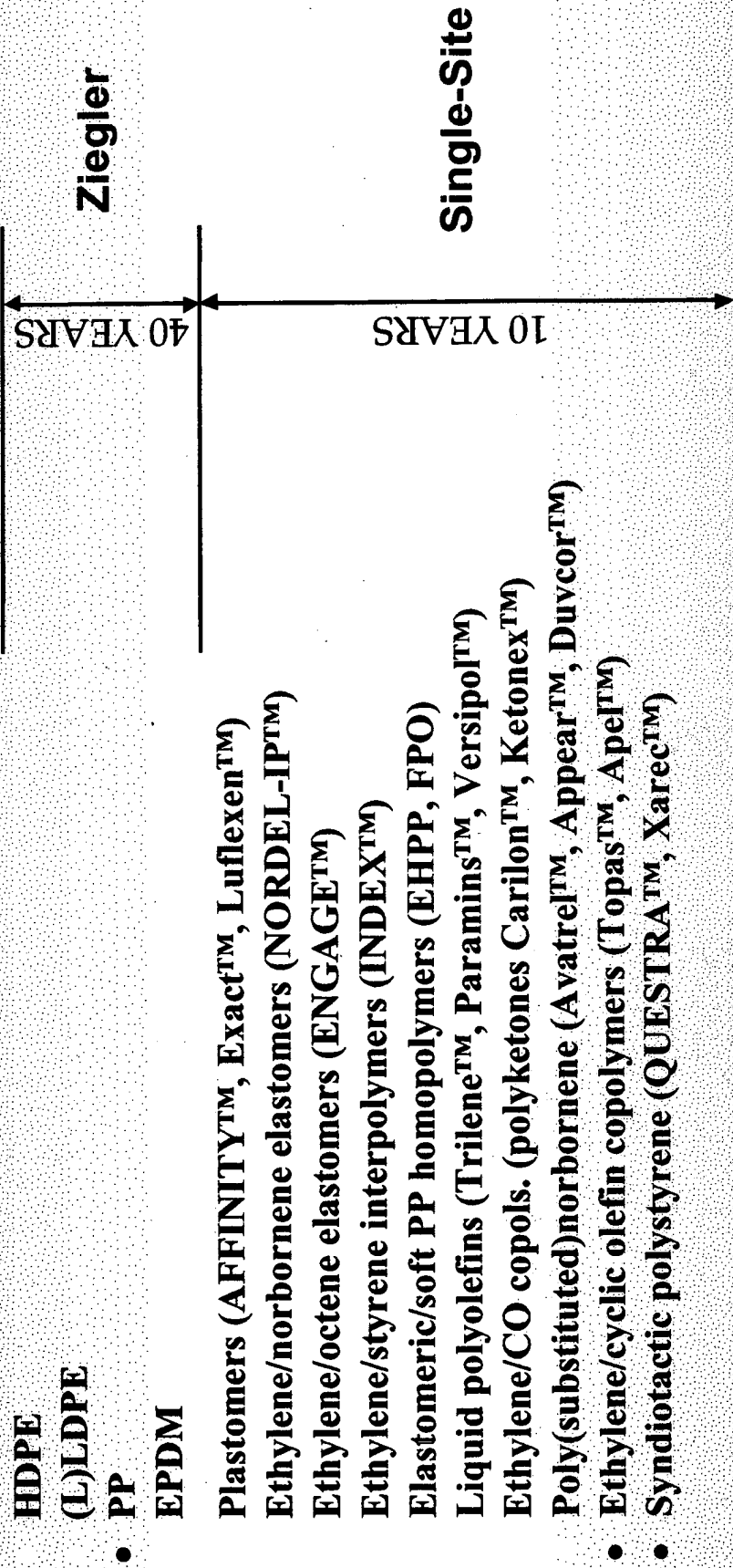


From this



To this

# The Rate of New Product Creation Has Been Faster With Single-Site Catalysts



Rate of New Market Creation. Source: STA\* research

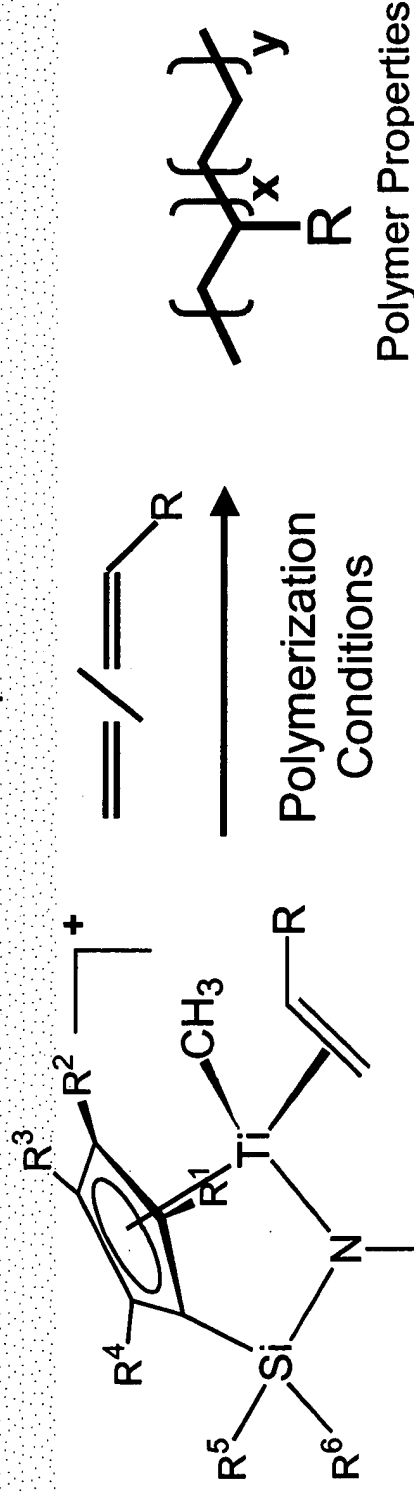


# **Single-Site Catalyst Discovery Research Centers On :**

- ❖ **More Productive Catalysts**
- ❖ **Higher Temperature Operation**
- ❖ **Higher Molecular Weights**
- ❖ **Higher Comonomer Contents**
- ❖ **Improved / Novel Control of Sequence Distributions**
- ❖ **Incorporation of New Comonomers**
- ❖ **Improved / Differentiated Products**
- ❖ **Novel Polymer Microstructures and Tacticity**

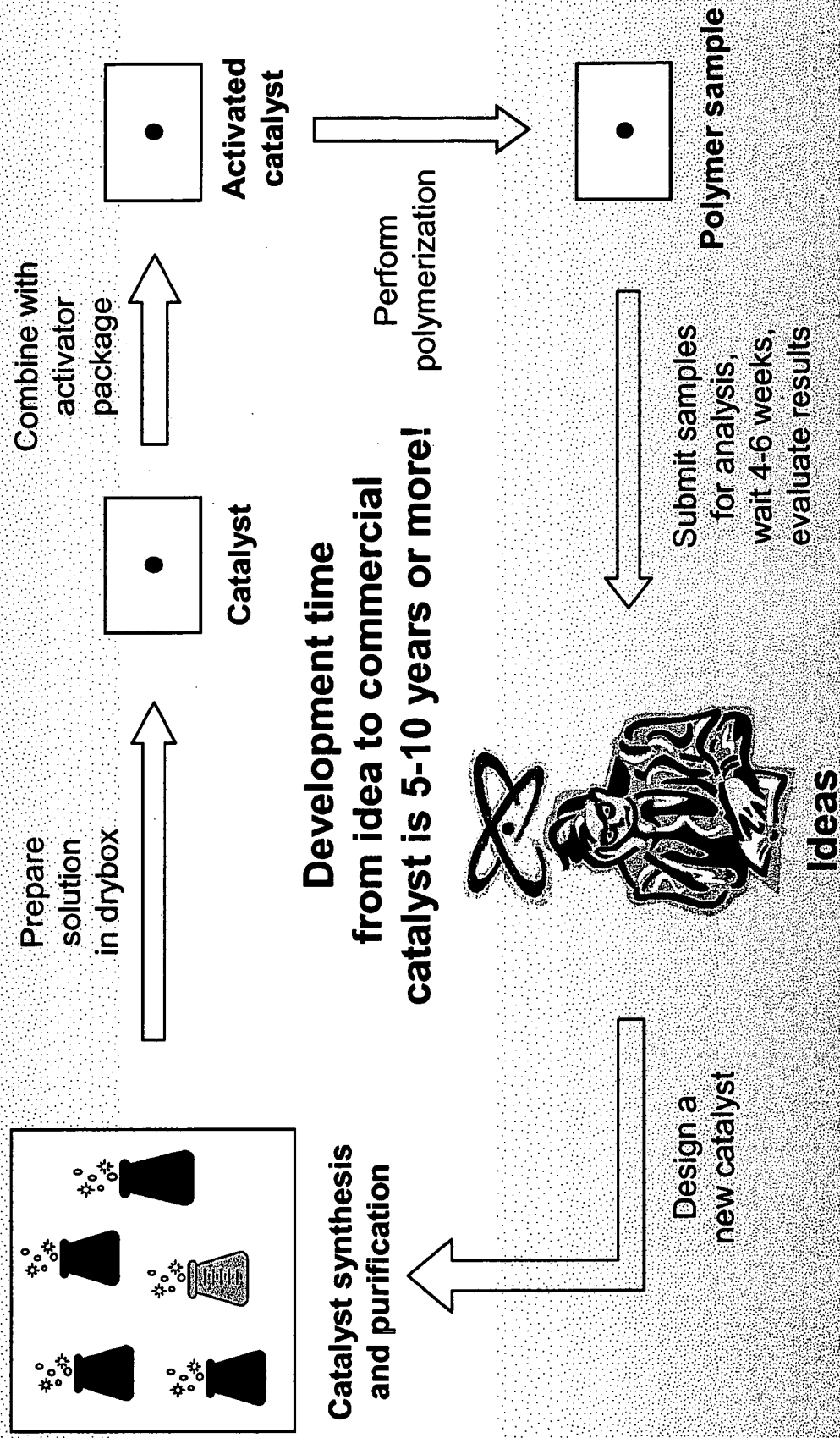
# Complete Evaluation of the Structure / Activity Relationships for any Catalyst Family is a Daunting Task

The Energy Surface for a Copolymerization is Highly Complex

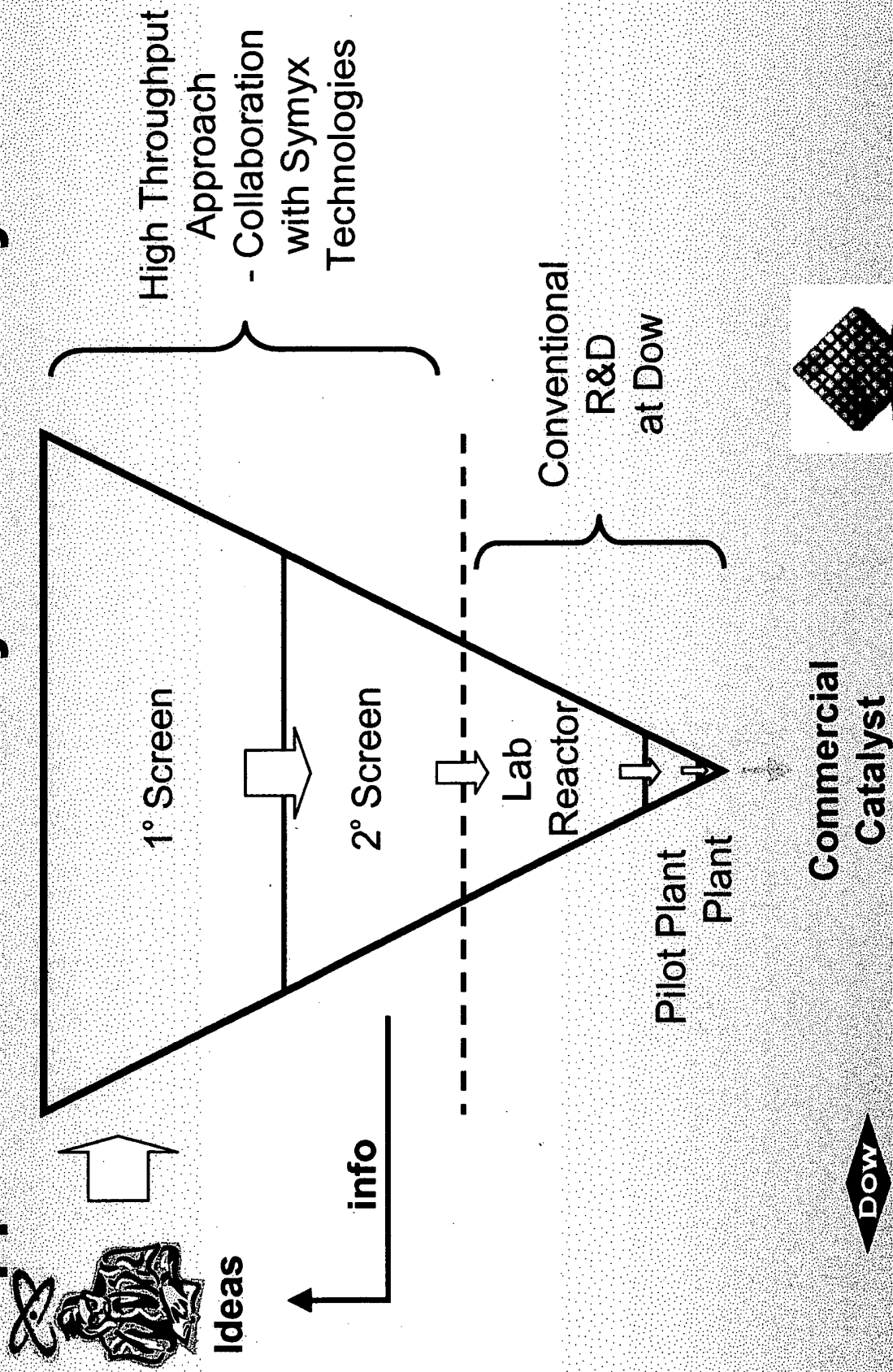


- 1) Properties of active site and polymer can be affected *dramatically and unpredictably* by variations in choice of Metal, Ligand(s), Activation Method and Process Conditions
- 2) Choosing Ten Substituents for Each Position on this ligand Generates around 10,000,000 Compounds !!!

# The Conventional Way of Doing Catalyst R&D is Effective But Can Be Slow



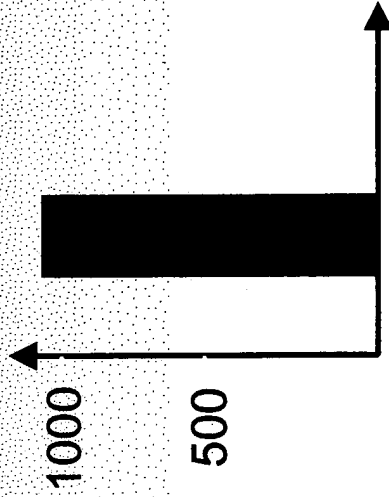
# Combinatorial and High-Throughput Approaches to Catalyst Discovery





# Experimental Throughput of Symyx / Dow Collaboration

Experiments per Day



“Discovery Screening”

High Throughput

Lower Precision

Yes/No Approach

Primary  
Screening

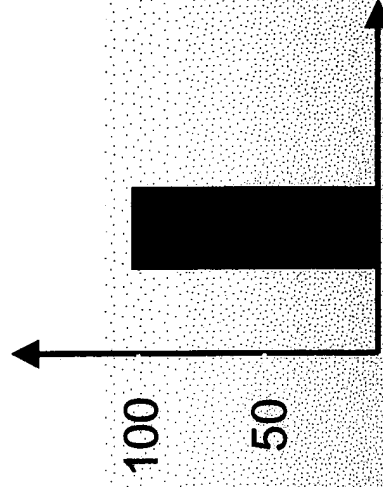
Hits and Information

“Optimization Screening”

Moderate Throughput

Higher Precision

Secondary  
Screening



“Experiment” means catalyst synthesis, polymerization, and analysis of performance, polymer properties, etc.

# High Throughput Catalyst Discovery Requires:

Large Number of Ligands with Suitable Diversity

Efficient Methods of Attaching Ligands to Metals

Comprehensive Activation Strategies

High Throughput **Primary** Screen

- Rapid analytical for activity, molecular weight, at smaller scales

High Throughput **Secondary** Screen

- Rapid analytical for activity, molecular weight, MWD, comonomer incorporation, tacticity, etc

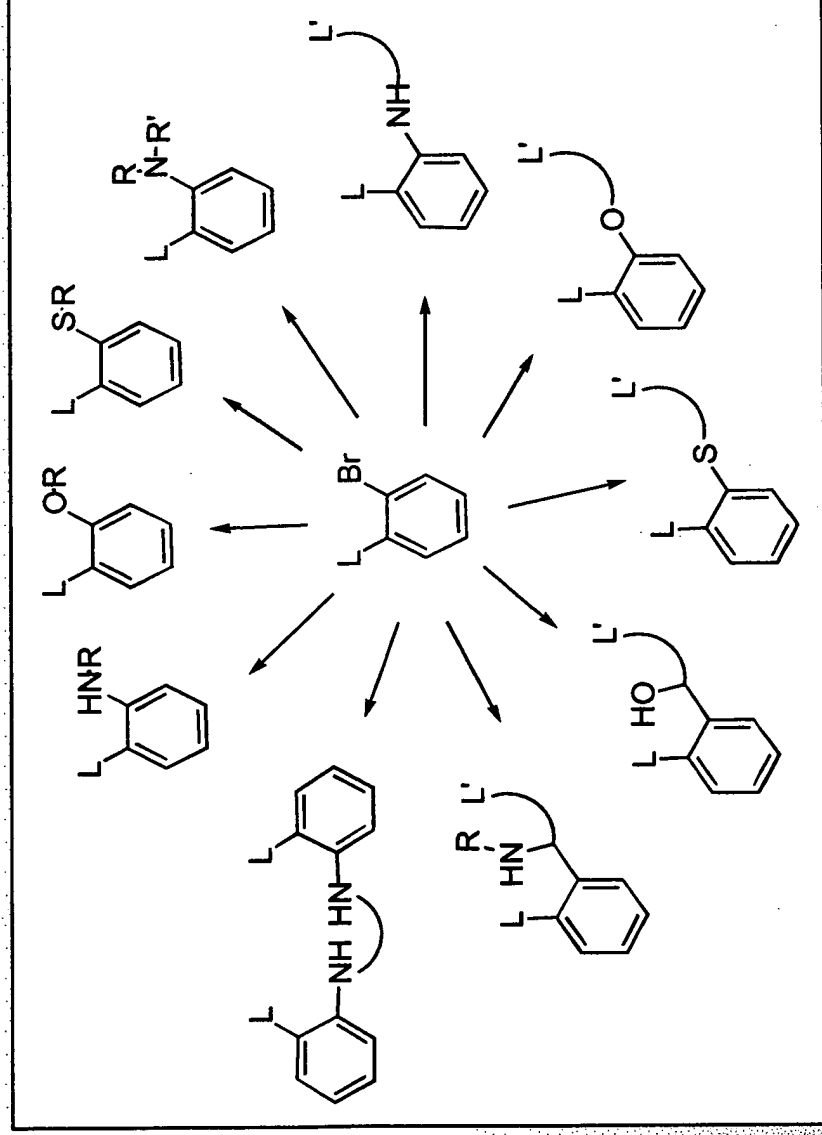


# Ligand Diversity: The Building Block Strategy

How can we exploit parallel synthesis techniques to create *diverse* ligand libraries?

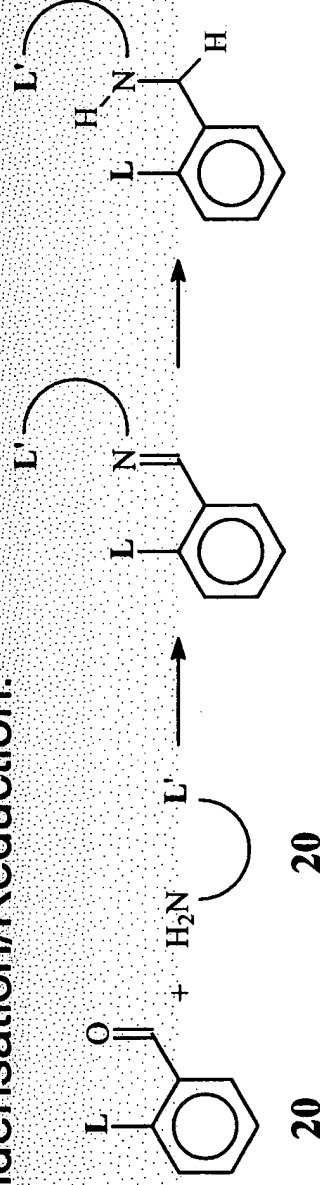
- Focus on post-metallocene catalyst systems
- Create diverse functionalized building blocks
- Connect building blocks using high-yield coupling reactions

# The Parallel Building-Block Approach Leads To Significant Diversity:

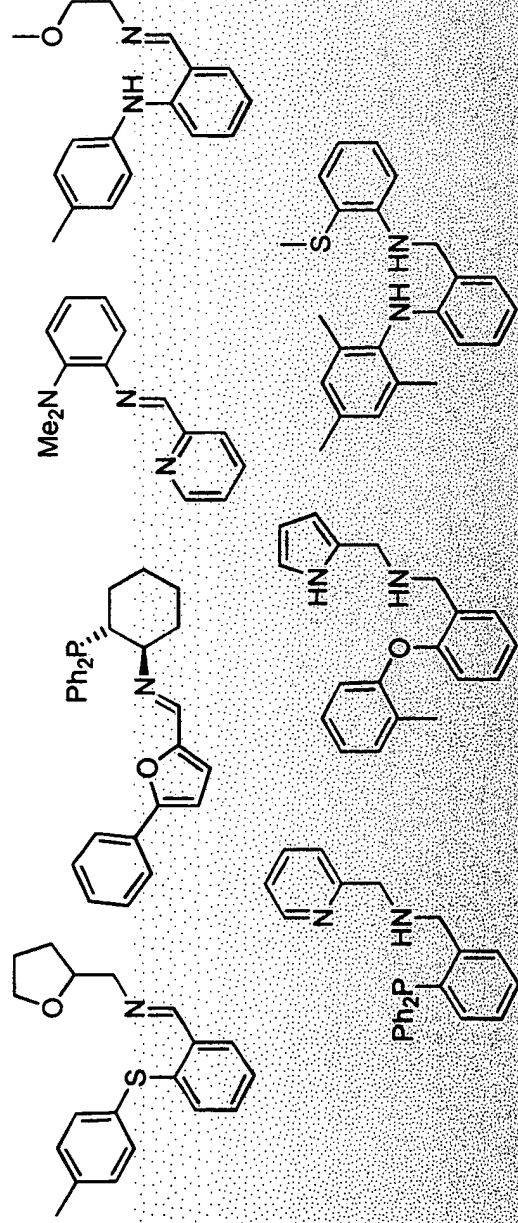


# One Example of Ligand Diversity via General Transformations

imine Condensation/Reduction:



$20 \times 20 \times 2 = 800$  Examples !!



800 ligands x 6 metals x 3  
monomers x 5 activators x  
3 temperatures = 216,000  
experiments!

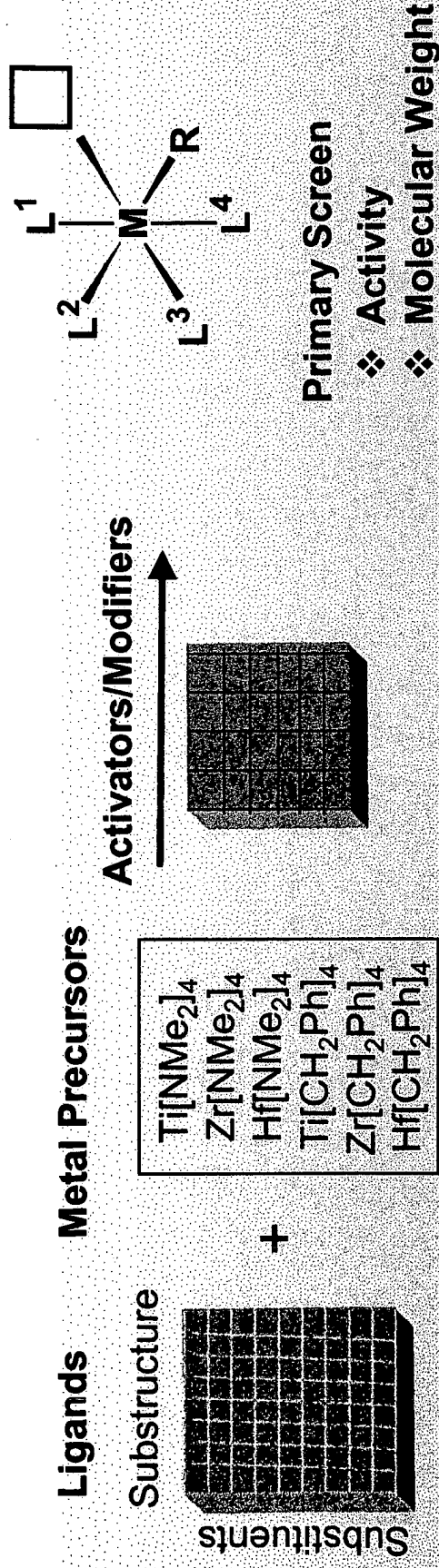
# Issues With Parallel Synthesis of Activated Metal Complexes

How can I rapidly ...

- Synthesize a diverse set of organometallic compounds, and
- know what I made, and
- select the appropriate activator?

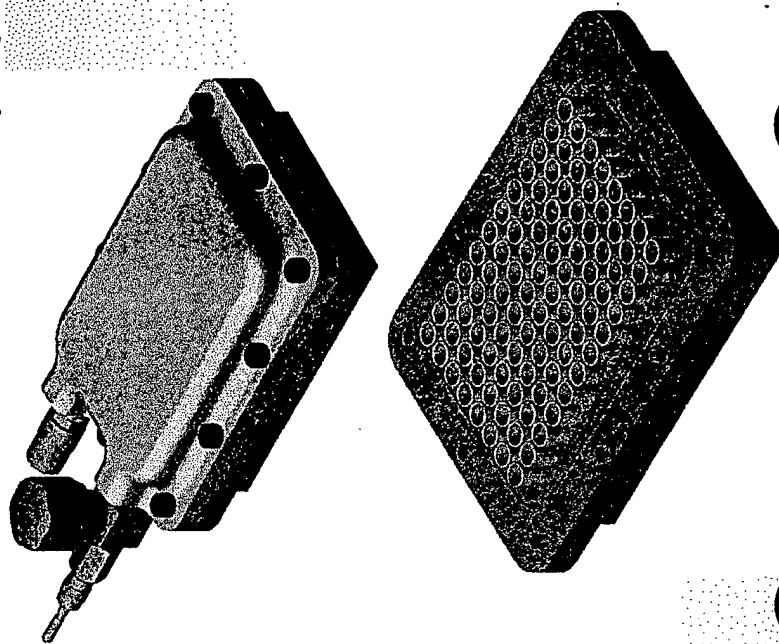
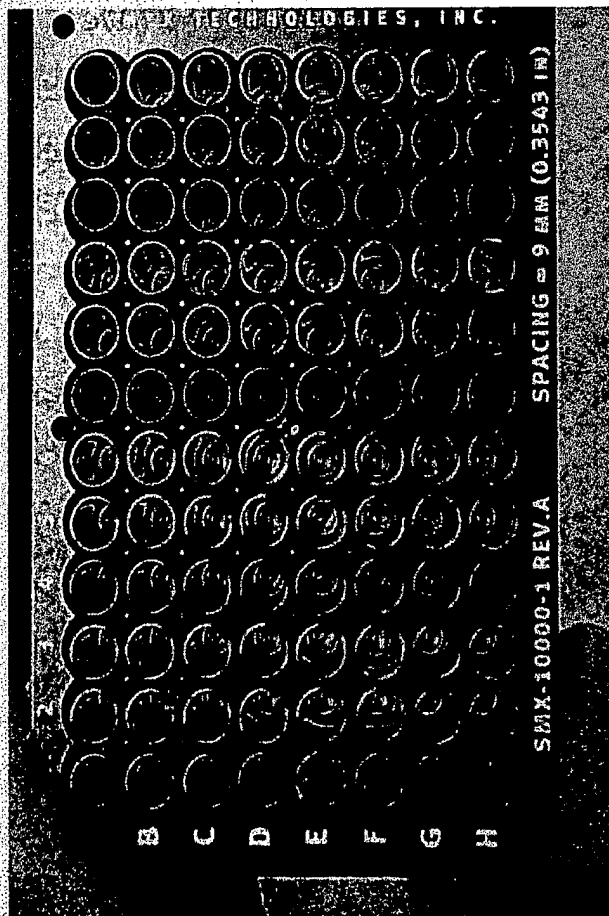
By ...

- accommodating multiple organometallic routes, and
- multiple activation chemistries for each metal / ligand set, and
- validating chemistry with models before experiment and for all hits

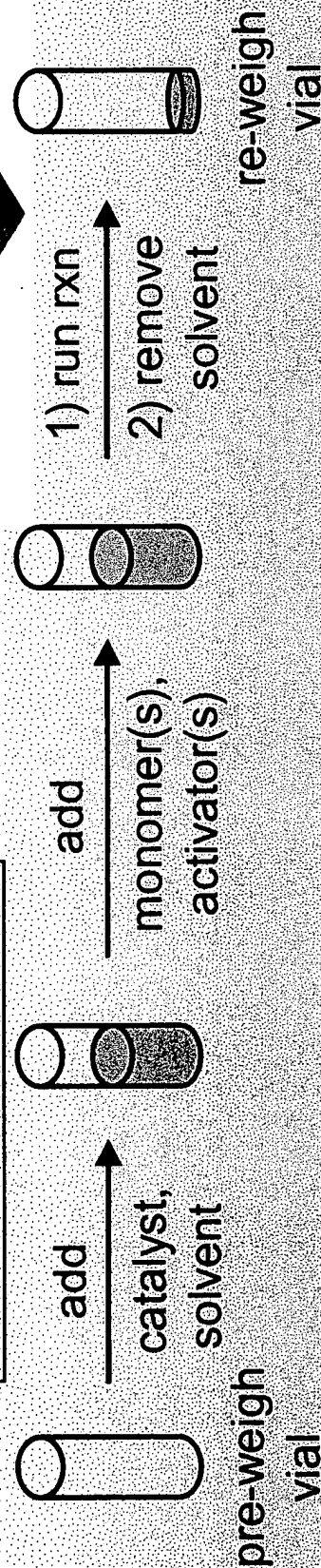




# Rapid Primary Screen Using Post Reaction Gravimetric Analysis

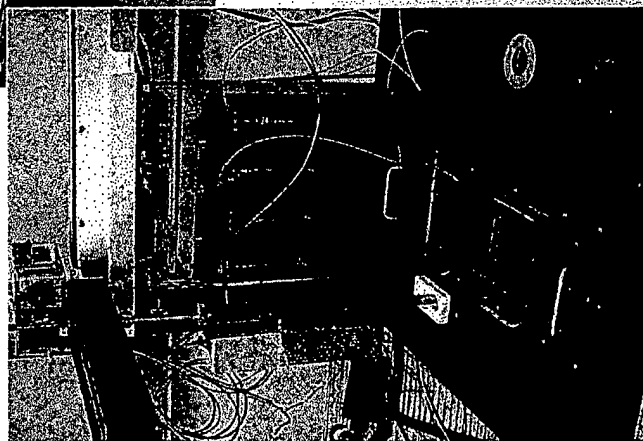
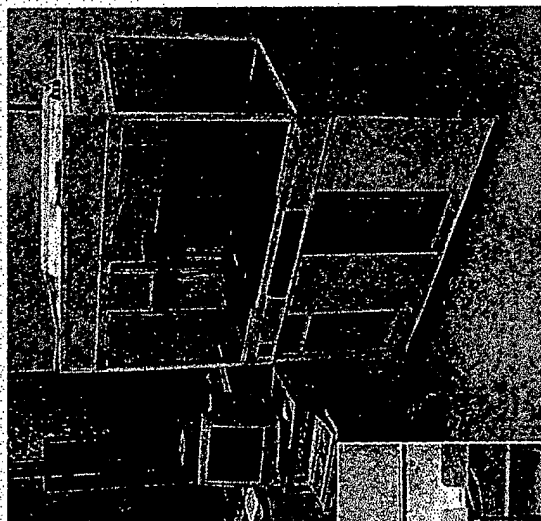


All Procedures Employ  
Robotic Liquid Handling

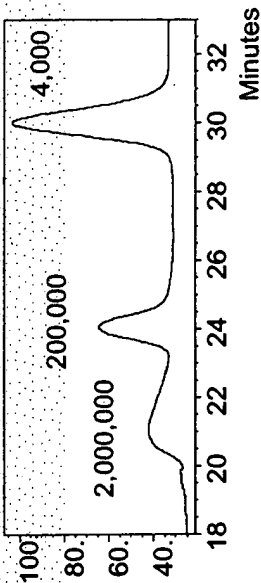


# High-Throughput Molecular Weight Measurements

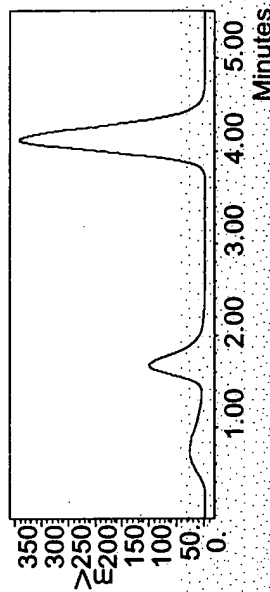
## Symyx Rapid GPC™



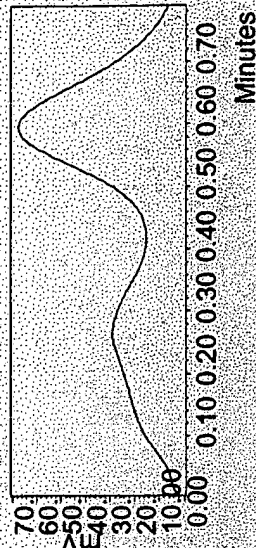
**Conventional (PL-GPC210)**



**High Resolution**

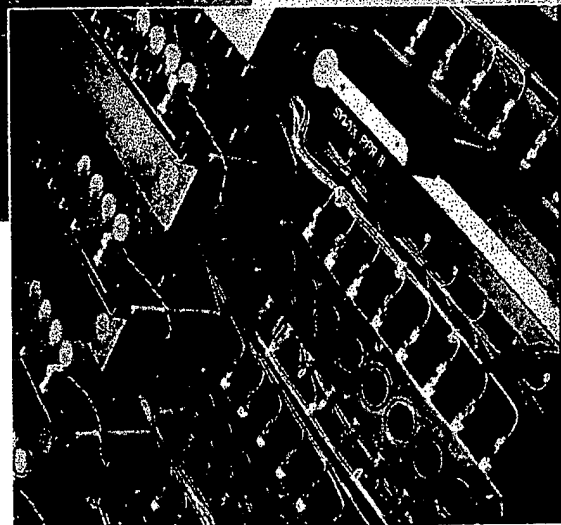


**High Throughput**

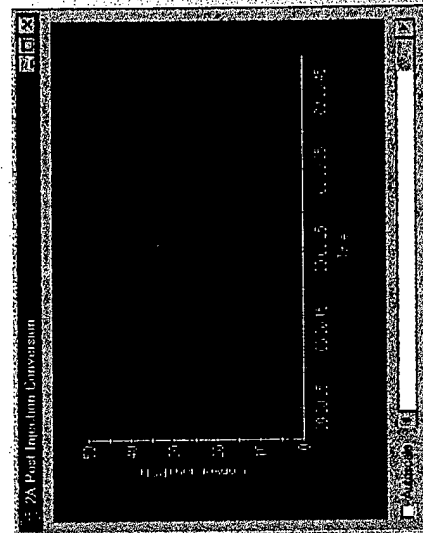
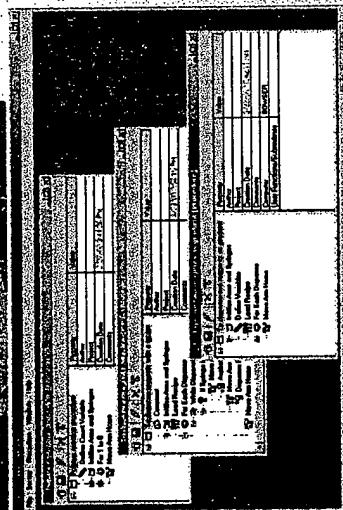




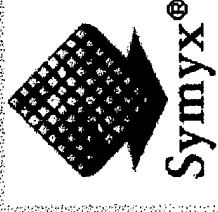
# Secondary Screening Tools Symyx Parallel Polymerization Reactor (PPR®)



- 48 reactions per run
- 6 mL reaction volume
- Reagents injected robotically at T and P
- Real-time monitoring
  - T, P and gas uptake in cell

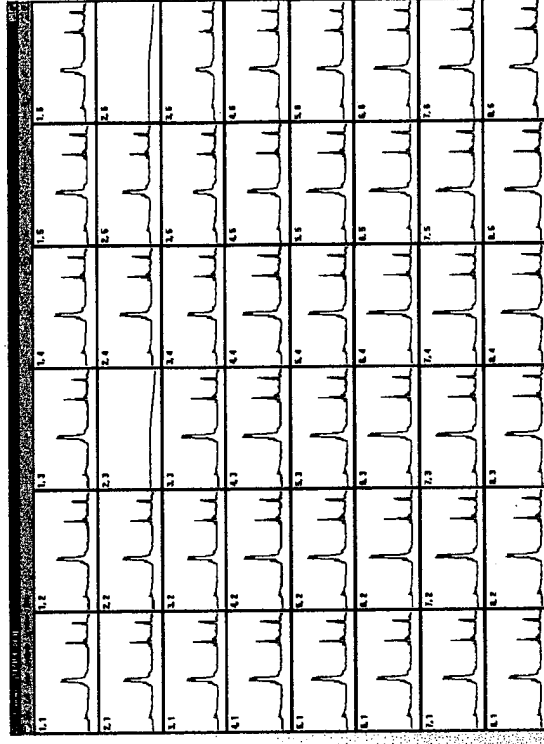
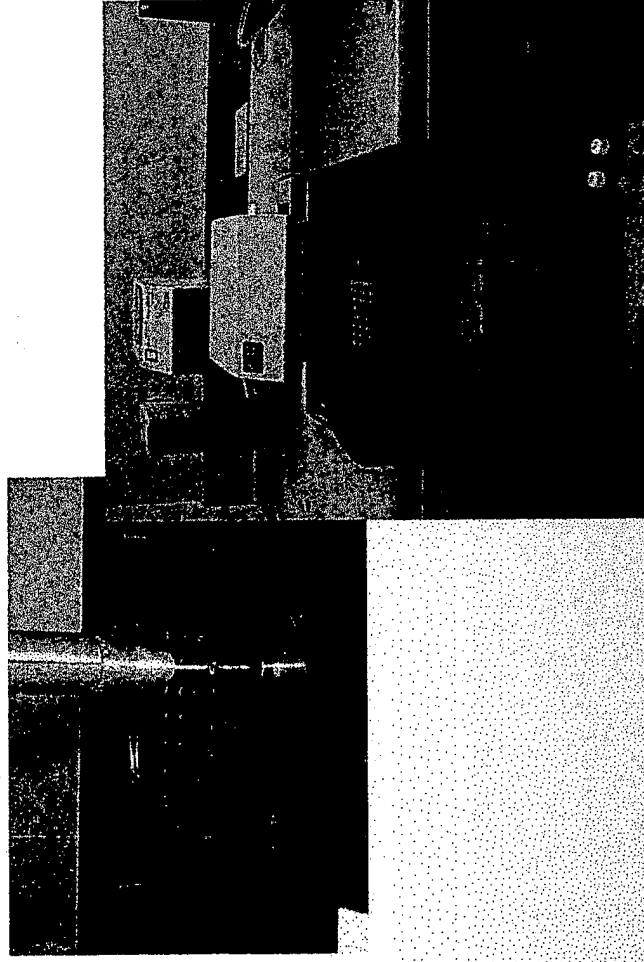


# Secondary Screening Analysis: FT-IR



IR spectra of polymers allows rapid analysis of:

- co-monomer composition
- tacticity

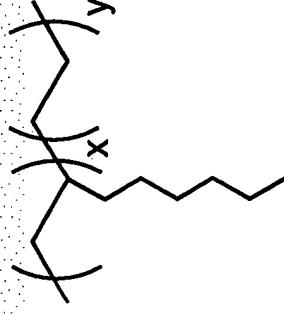


Automated Reflection FT-IR Analysis of Polymer Films

# A Case Study of High-Throughput Catalyst Discovery

Target: High Temperature Solution Phase LLDPE Catalyst

- ❖ Catalyst must operate at temperatures > 130 °C
- ❖ Requires high activity, high  $M_w$ , high 1-octene incorporation



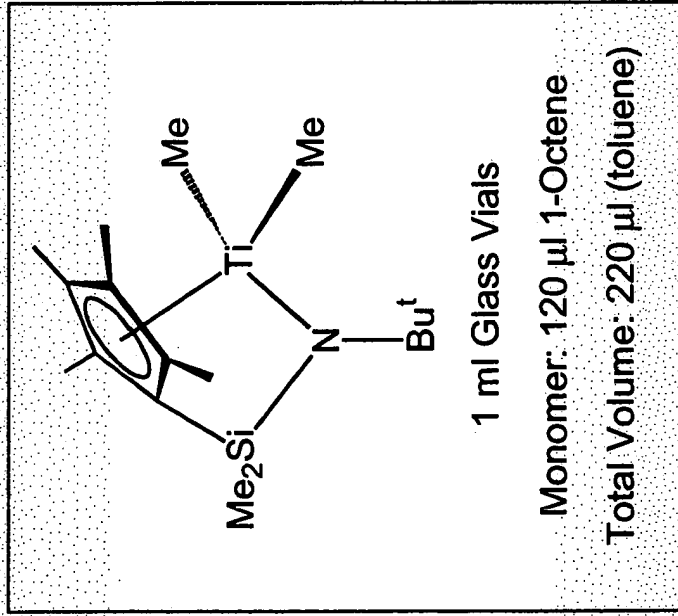
**Primary Screen:**  
1-Octene Polymerization Activity

Hits and Information

1-Octene Polymerization Capability

**Secondary Screen:**  
High Temperature Ethylene/ 1-Octene Screen

# Adaption to Small Scale: Primary Screening Validation



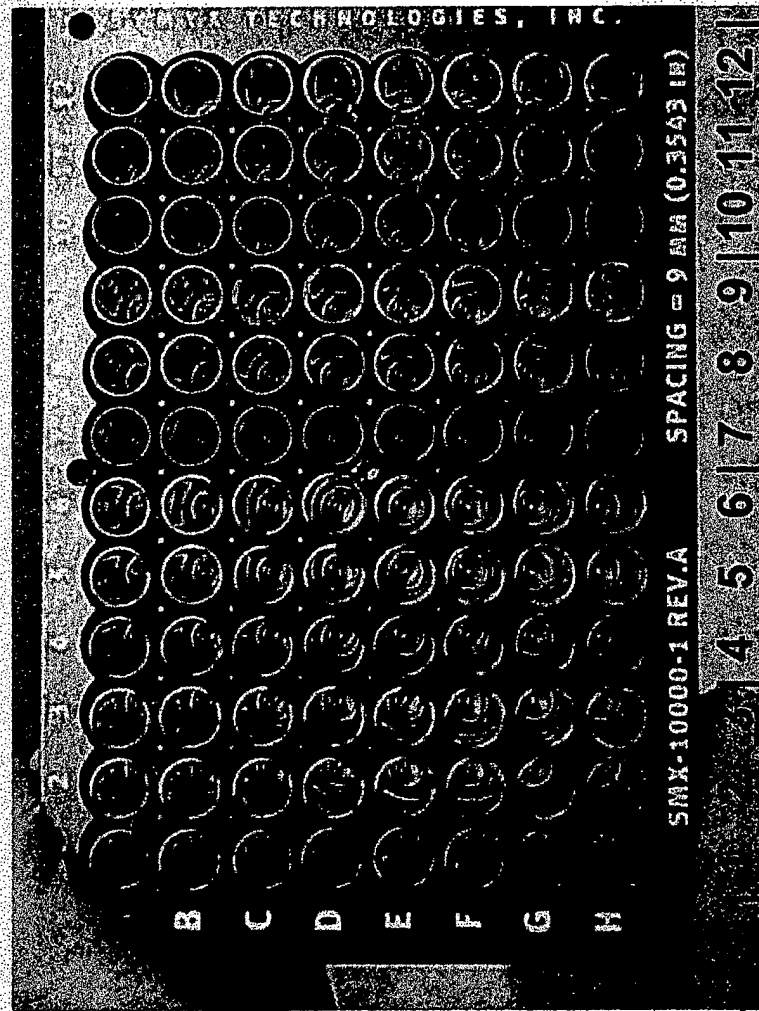
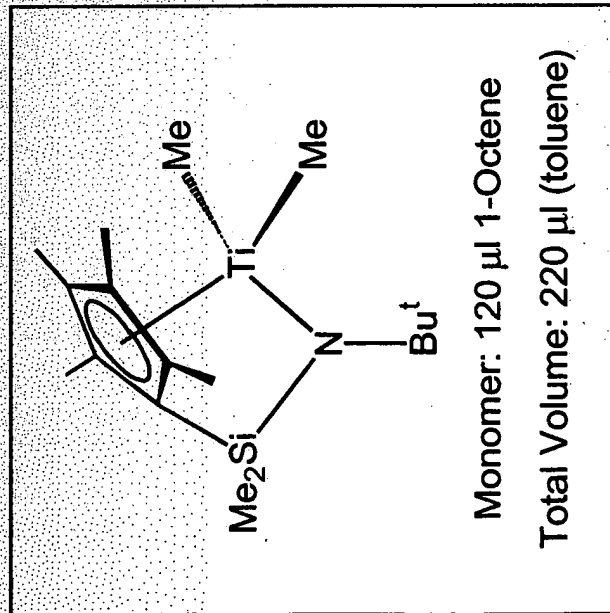
[8 x 12] Array

3 Catalyst Concentrations  
4 Activation Methods  
8 Replicates of Each  
Condition

Use robots to dispense  
reagents and to analyze  
products for speed, accuracy



# Adaption to Small Scale: Primary Screening Validation



8  
Replicates

Column No.

4 Activation  
Zones

3 Catalyst  
Concentrations  
(mM)

None (Control)				200 eq. MAO				[Me <sub>2</sub> PhNH] <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>				[Me <sub>2</sub> PhNH] <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> + 5 eq. Bu <sup>i</sup> <sub>3</sub> Al			
1.8	0.18	0.018	0.0018	1.8	0.18	0.018	0.0018	1.8	0.18	0.018	0.0018	1.8	0.18	0.018	0.0018

# Adaption to Small Scale: Primary Screening Validation Procedure

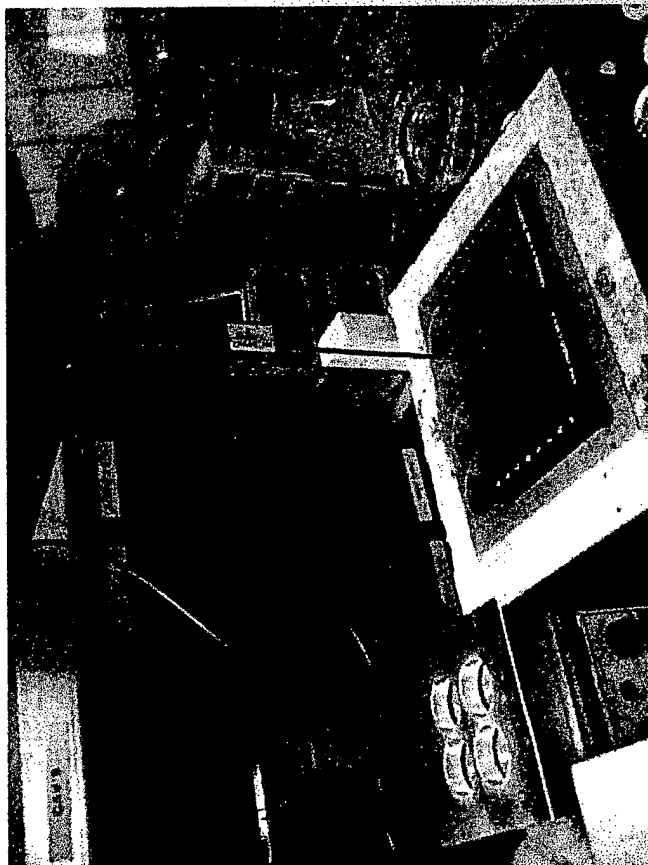


1. Add 120  $\mu\text{L}$  1-Octene.
2. Add  $\text{Bu}^i_3\text{Al}$  to columns 10, 11, 12.
3. Add  $[(\eta^5\text{-C}_5\text{Me}_5)\text{SiMe}_2(\eta^1\text{-NBu}^t)]\text{TiMe}_2$ .
4. Add Activators.



1. Run Polymerization
2. Quench, Filter
3. Automated Dilution
4. Rapid GPC<sup>TM</sup>
5. Obtain  $M_w$ , Conversion

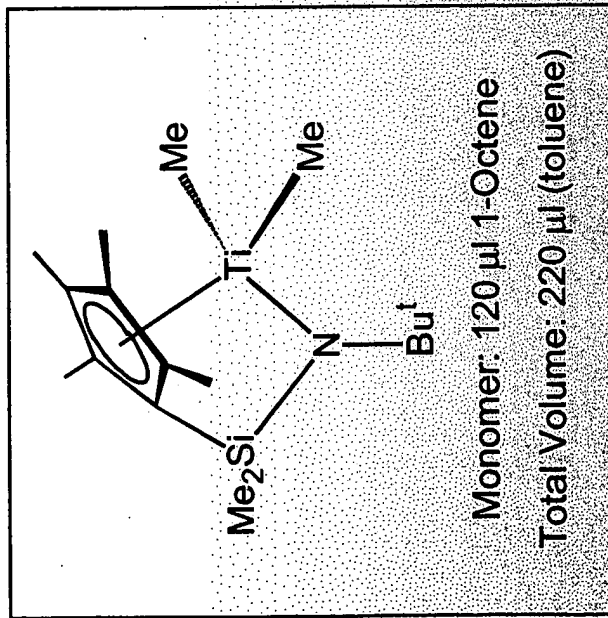
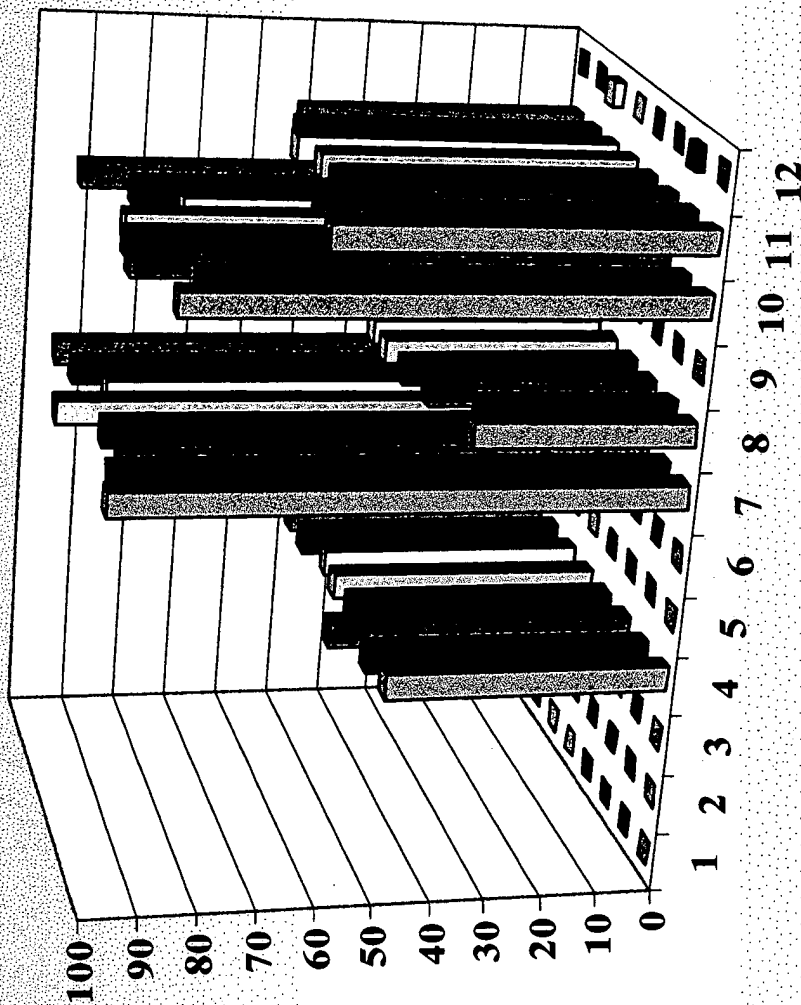
All Procedures Employ  
Robotic Liquid Handling





# Adaption to Small Scale: Primary Screening Catalyst Activity Validation

% Conversion  
to Poly-1-Octene

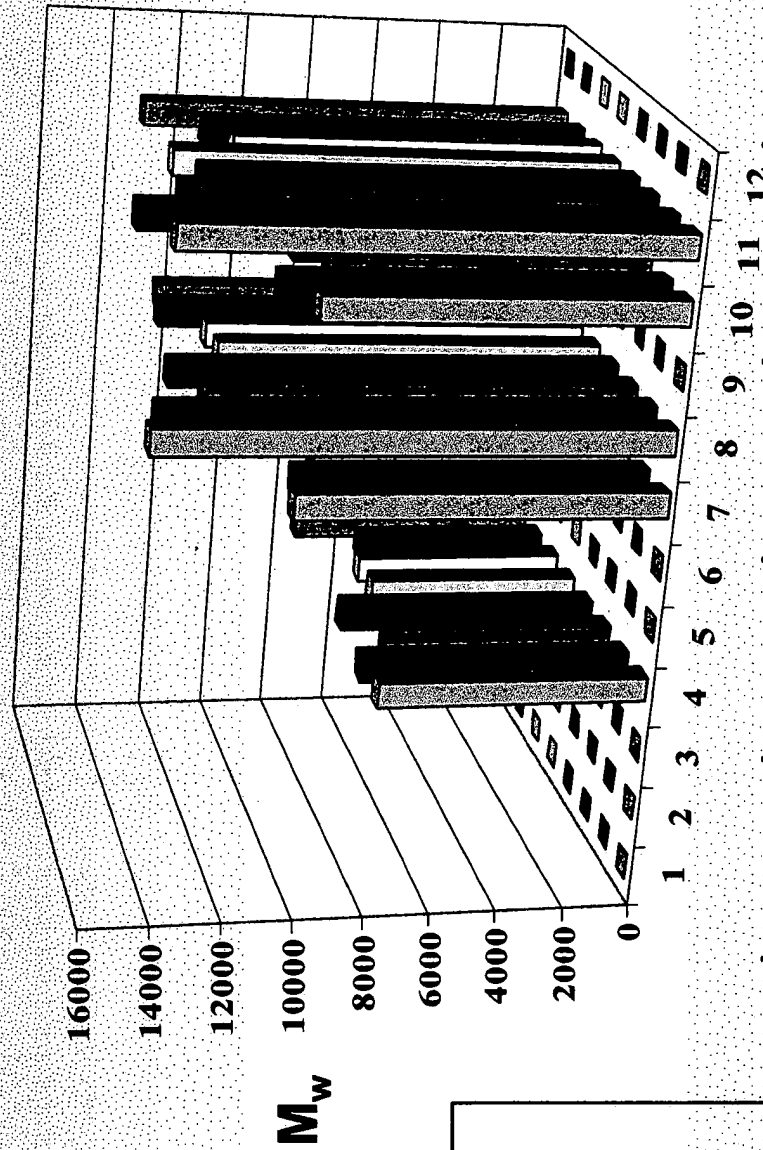


None	200 eq. MAO	[Me <sub>2</sub> PhNH] <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> + 5 eq. Bu <sup>t</sup> Al		
1.8	0.18	0.18	1.8	0.18
0.18	0.18	1.8	0.18	0.18
0.18	0.18	1.8	0.18	0.18

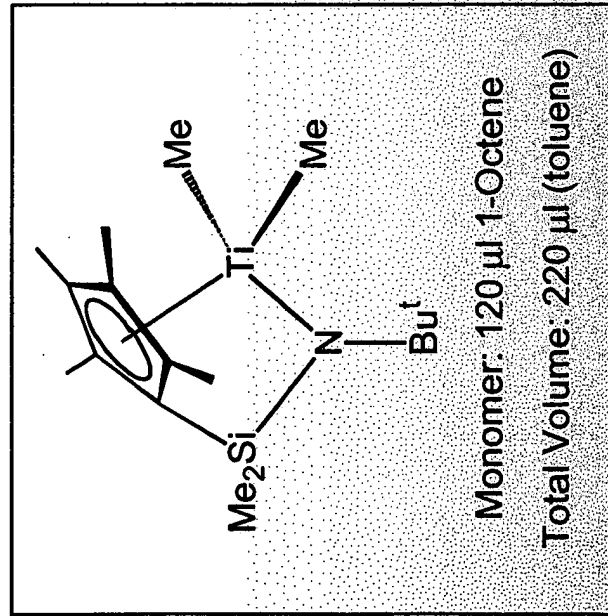
3 Catalyst  
Concentrations  
(mM)

# Adaption to Small Scale: Primary Screening

## Mw Validation



$M_w$



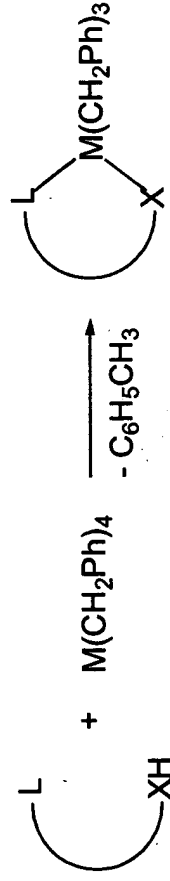
None			200 eq. MAO			[Me <sub>2</sub> PhNH] <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>			[Me <sub>2</sub> PhNH] <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> + 5 eq. Bu <sup>t</sup> Al		
1.8	0.18	0.18	1.8	0.18	0.18	1.8	0.18	0.18	1.8	0.18	0.18

3 Catalyst  
Concentrations  
(mM)

# Catalyst Discovery Screening

- Adaption of the Chemistry to Smaller Scale
- Large Number of Ligands with Suitable Diversity
- Efficient Methods of Attaching Ligands to Metals
- Suitable Rapid Screening Technique

The Use of Acidic ligands with  $M(\text{CH}_2\text{Ph})_4$  ( $M = \text{Zr, Hf}$ ) and Multiple Activation Conditions



$M(\text{CH}_2\text{Ph})_4$   
( $M = \text{Zr, Hf}$ )

1 Hour, Toluene

Ligand/ $M(\text{CH}_2\text{Ph})_4$   
Mixtures

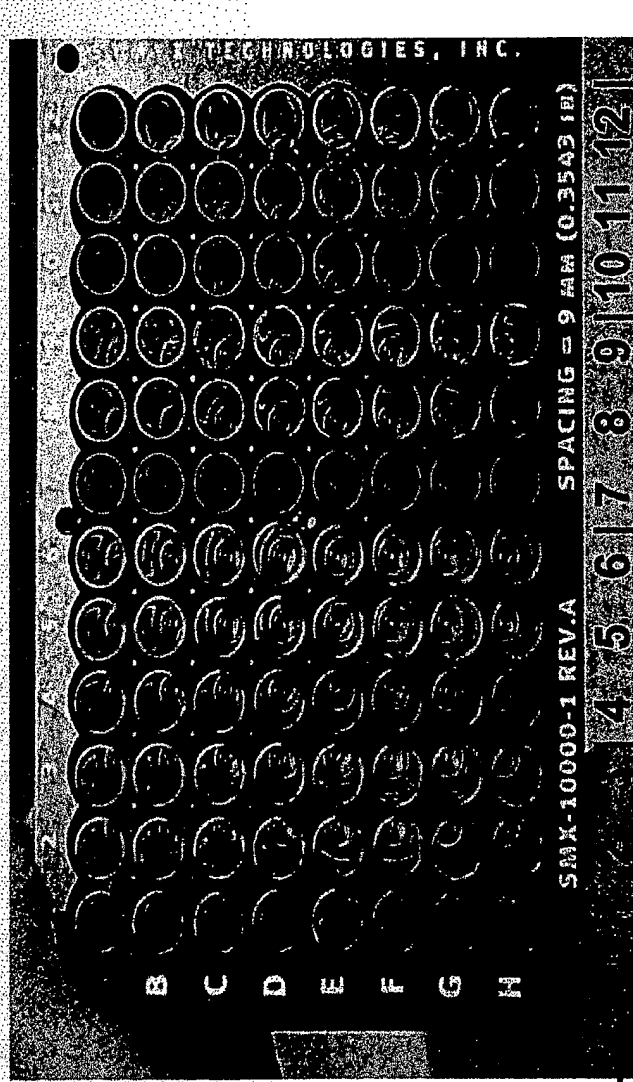
Multiple Activation  
Conditions

[3 x 8] Set of  
Charged Ligands

# Catalyst Discovery Screening - Plate Design

## Discovery Plate Design

Eight Activation  
Conditions for Each  
Ligand/ $M(CH_2Ph)_4$   
Combination  
- 2 plates of 4  
conditions



Column No.

Activation  
Zones

Ligand/ $M(CH_2Ph)_4$   
Concentration  
(mM)

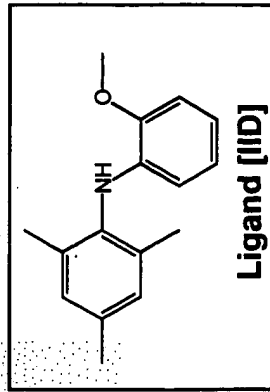
$[Ph_3C]^+$ $[B(C_6F_5)_4]^-$ + 5 eq. $Et_3Al$	$[Ph_3C]^+$ $[B(C_6F_5)_4]^-$ + 5 eq. $Bu^i_3Al$	$[Me_2PhNH]^+$ $[B(C_6F_5)_4]^-$ + 5 eq. $Et_3Al$	$[Me_2PhNH]^+$ $[B(C_6F_5)_4]^-$ + 5 eq. $Bu^i_3Al$	1 ↓ 8
1.6	1.6	1.6	1.6	

4 Zones each containing [3 x 8] Ligand Set

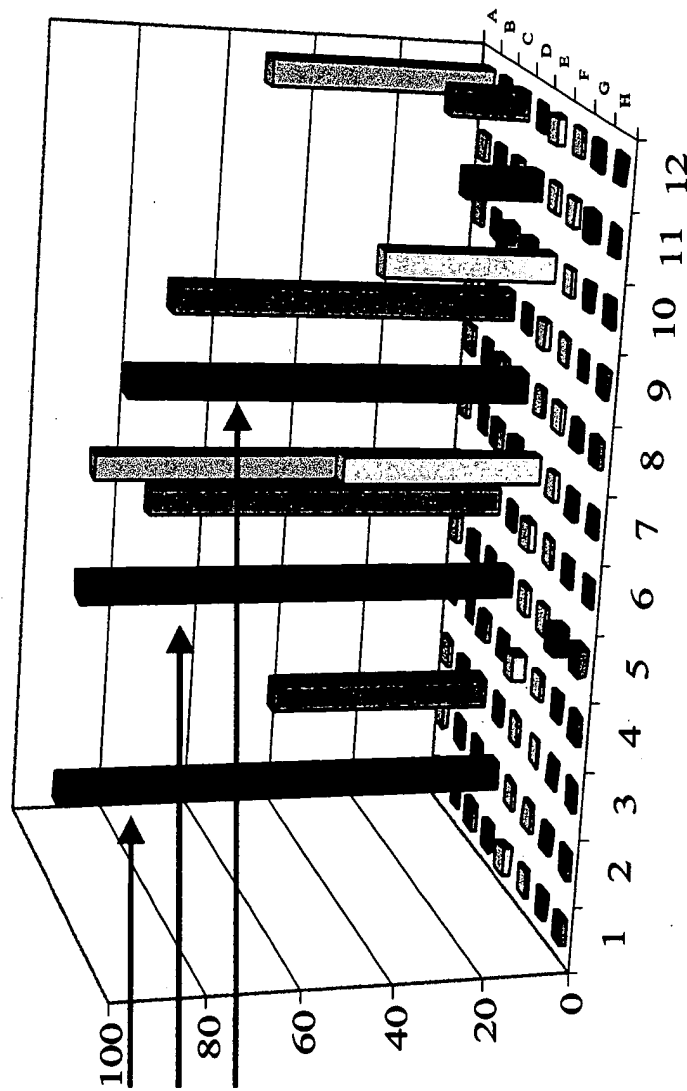


# Catalyst Discovery Screening - Activity Results

% Conversion Data  
Hf(CH<sub>2</sub>Ph)<sub>4</sub>



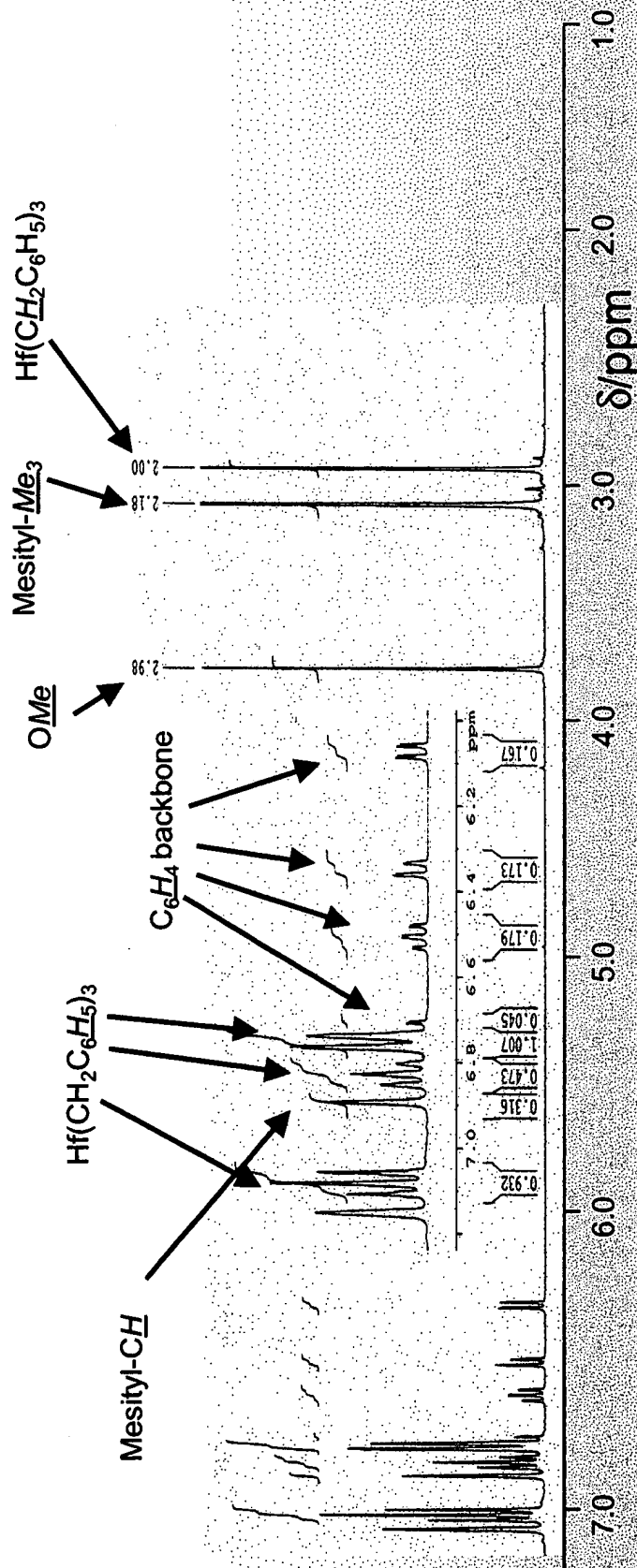
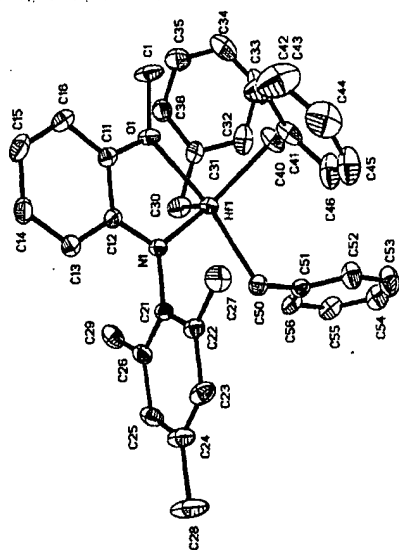
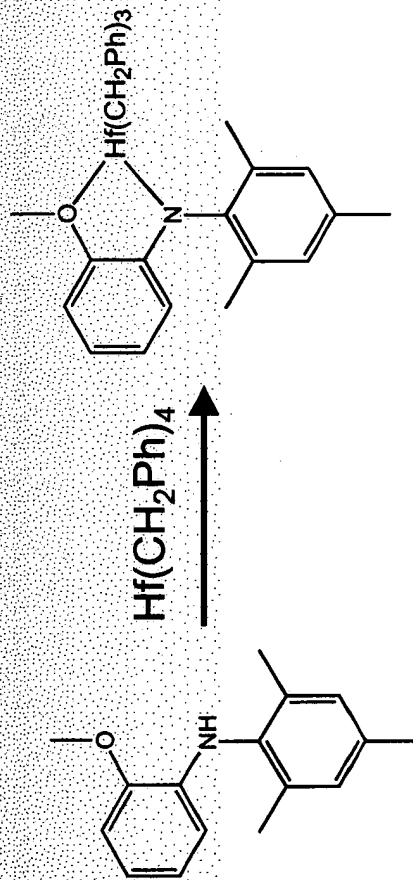
% Conversion  
to Poly-1-Octene



[Me <sub>2</sub> PhNH] <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> + 5 eq. Et <sub>3</sub> Al	[Me <sub>2</sub> PhNH] <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> + 5 eq. Bu <sub>13</sub> Al	[Ph <sub>3</sub> C] <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> + 5 eq. Et <sub>3</sub> Al	[Ph <sub>3</sub> C] <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> + 5 eq. Bu <sup>1</sup> <sub>3</sub> Al
1.6	1.6	1.6	1.6

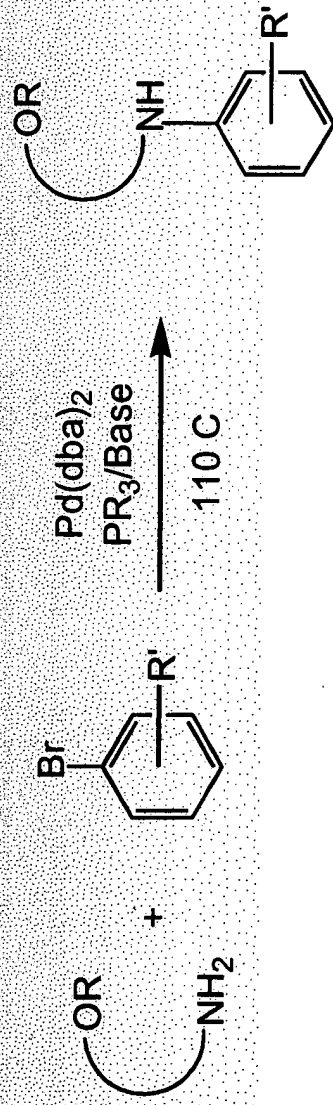
Ligand/Hf(CH<sub>2</sub>Ph)<sub>4</sub>  
Concentration  
(mM)

# After Hit Identification, Conventional Chemistry Identifies Structure of Active Catalyst



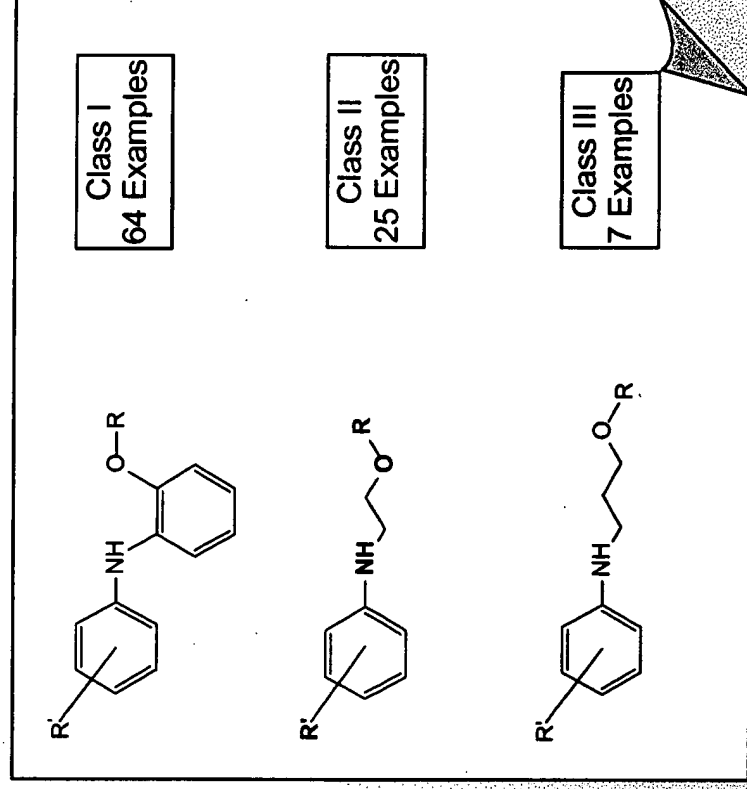
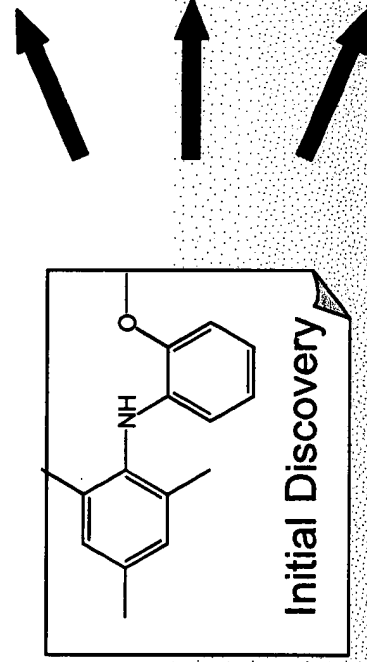


# Focus Library of Structural Variation Around Identified Hit

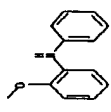
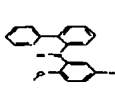
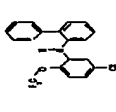
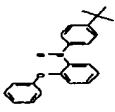
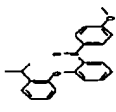
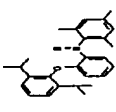
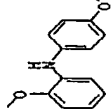
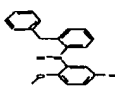
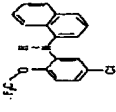
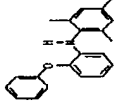
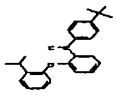
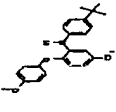
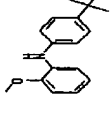
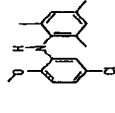
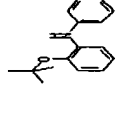
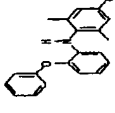
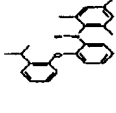
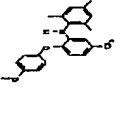
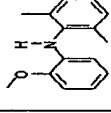
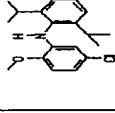
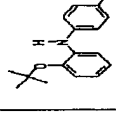
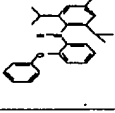
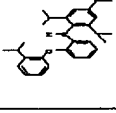
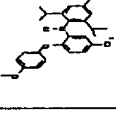
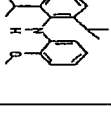
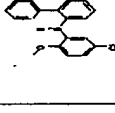
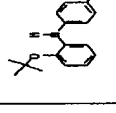
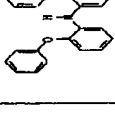
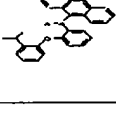

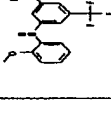
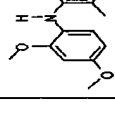
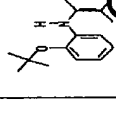
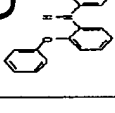
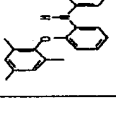

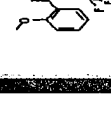
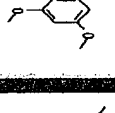
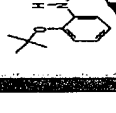
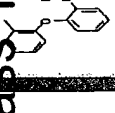
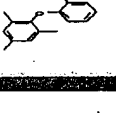

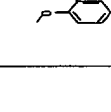
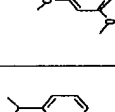
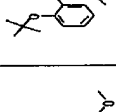
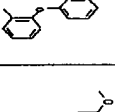
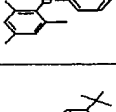

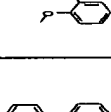
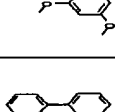
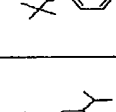
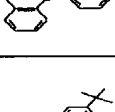
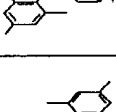

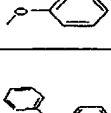
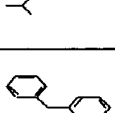
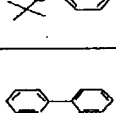
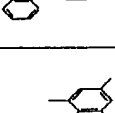
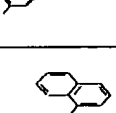

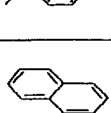
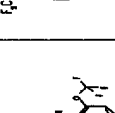
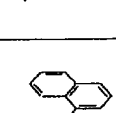
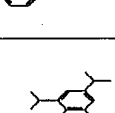
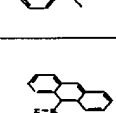

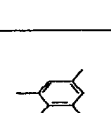
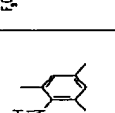
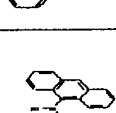
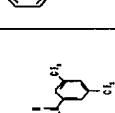
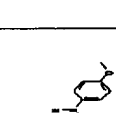

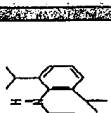
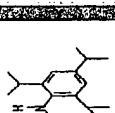
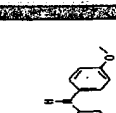
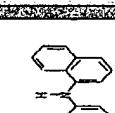
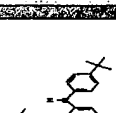

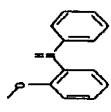
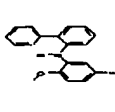
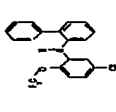
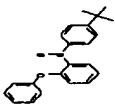
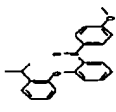
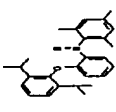
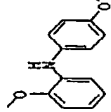
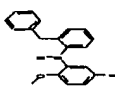
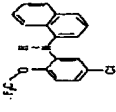
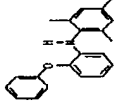
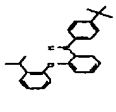
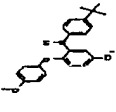
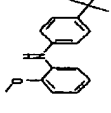
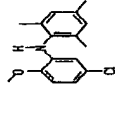
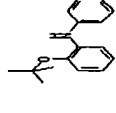
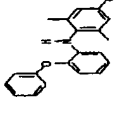
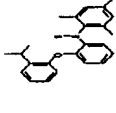
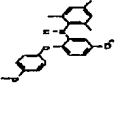
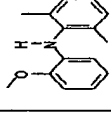
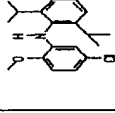
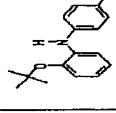
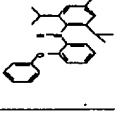
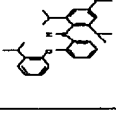
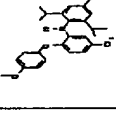
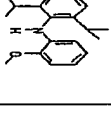
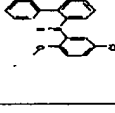
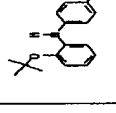
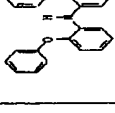
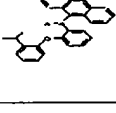

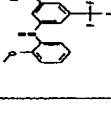
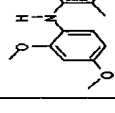
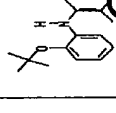
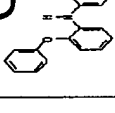
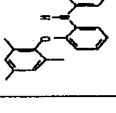

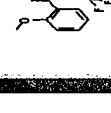
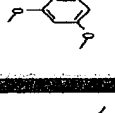
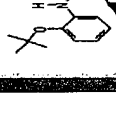
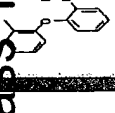
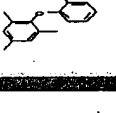

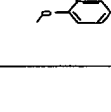
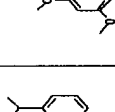
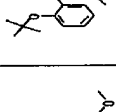
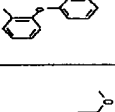
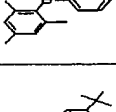

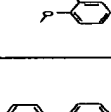
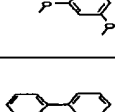
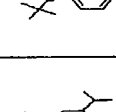
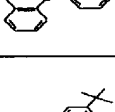
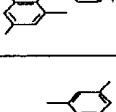

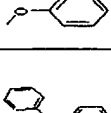
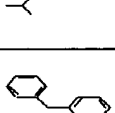
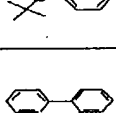
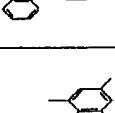
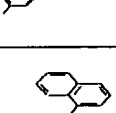

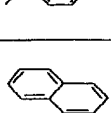
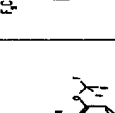
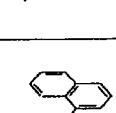
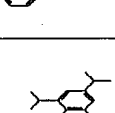
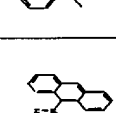

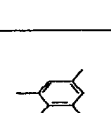
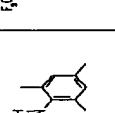
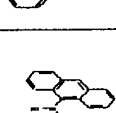
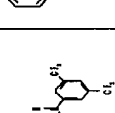
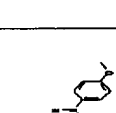

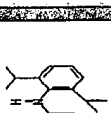
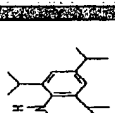
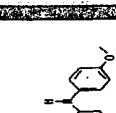
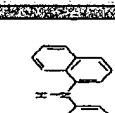
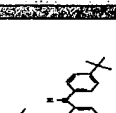

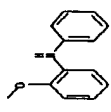
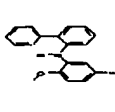
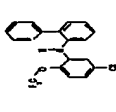
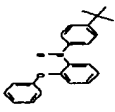
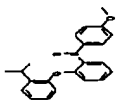
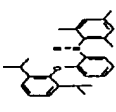
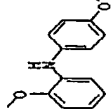
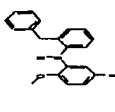
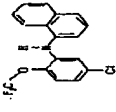
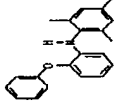
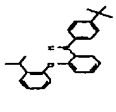
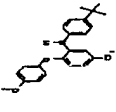
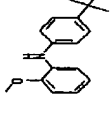
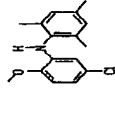
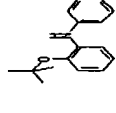
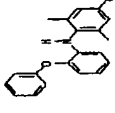
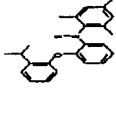
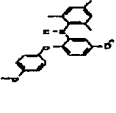
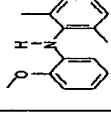
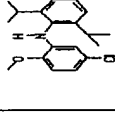
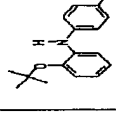
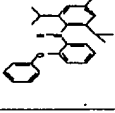
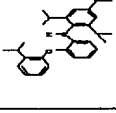
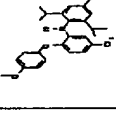
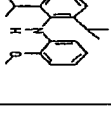
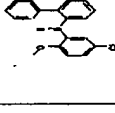
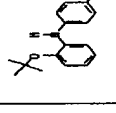
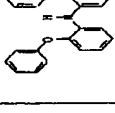
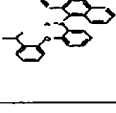

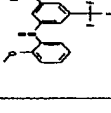
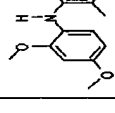
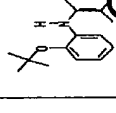
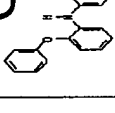
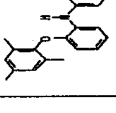

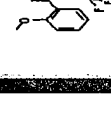
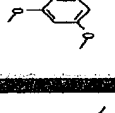
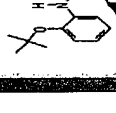
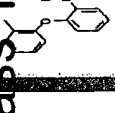
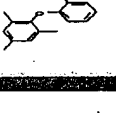

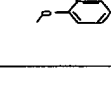
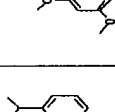
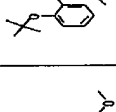
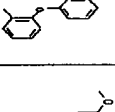
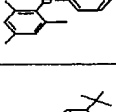

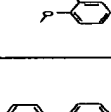
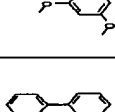
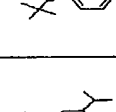
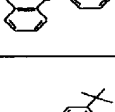
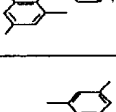

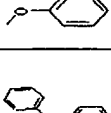
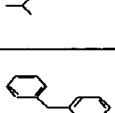
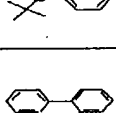
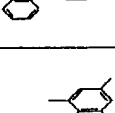
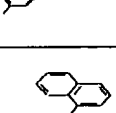

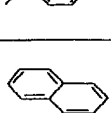
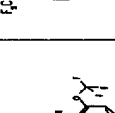
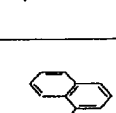
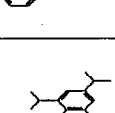
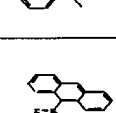

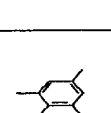
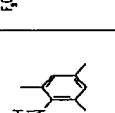
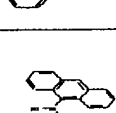
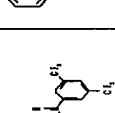
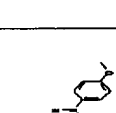

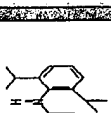
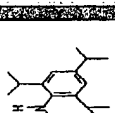
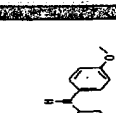
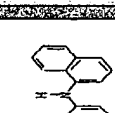
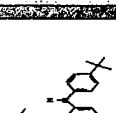



## Focus Library Preparation

❖ 96 Structural Variations



# Focus Library for Amine Ether Hit

					
					
					
					
					
					
					
					
					
					
					
					
					
<b>Class 1</b>					
					
					
					
					
					
					
					
					
					
					
					
					
					
<b>Class 2</b>					
					
					
					
					
					
					
					
					
					
					
					
					
					
<b>Class 3</b>					

# Secondary Screening

## 96 High Temperature Ethylene-Octene Copolymerizations

### Reactor Conditions

130 °C, 100 psi Ethylene

6.1 mL Total (Toluene)

0.25 mL 1-Octene

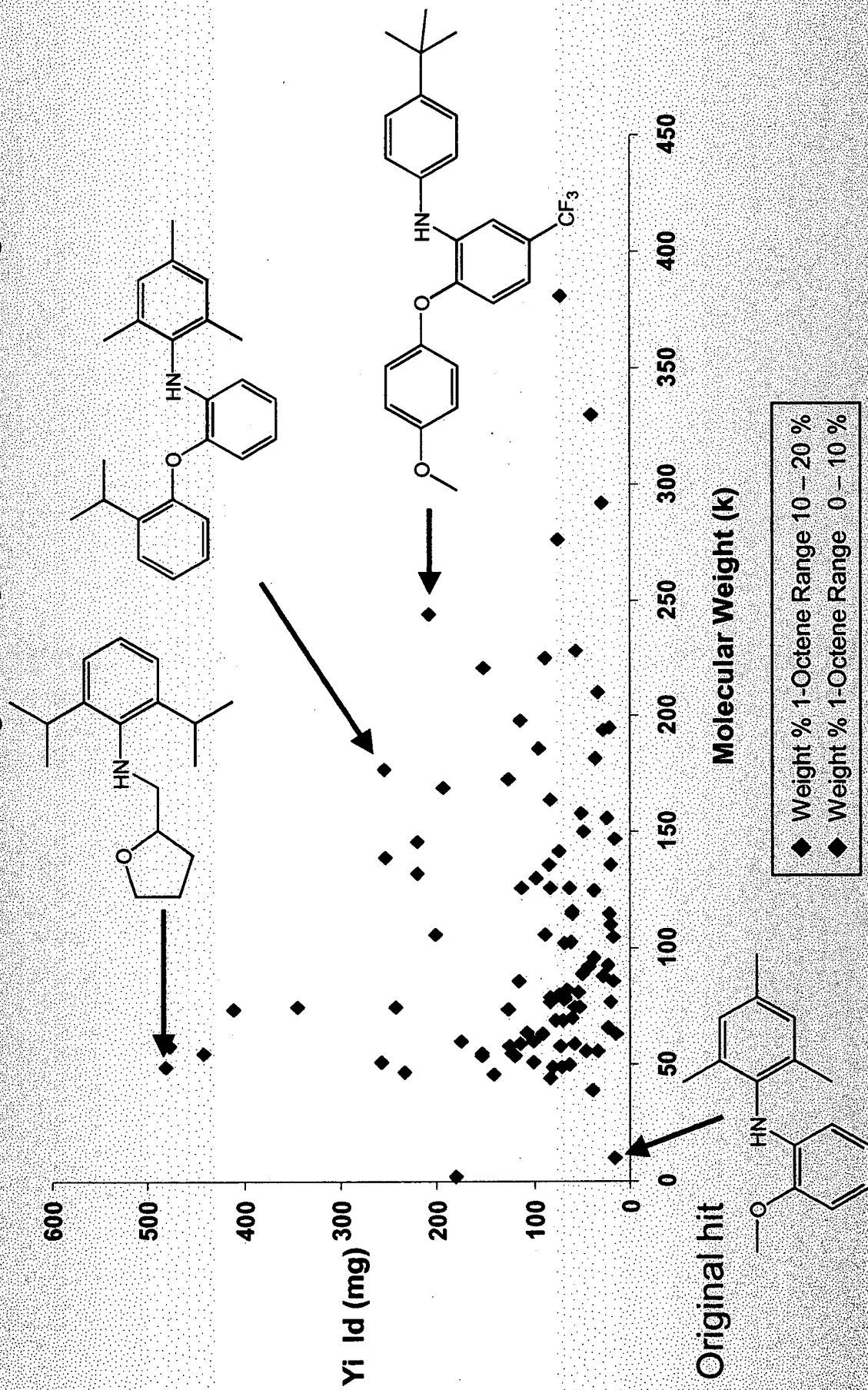
2  $\mu\text{mol}$   $\text{Bu}^i_3\text{Al}$

1  $\mu\text{mol}$   $\text{Hf}(\text{CH}_2\text{C}_6\text{H}_5)_4/\text{Ligand}$

Target:  
200-300 mg Copolymer

- |                     |   |                 |   |   |
|---------------------|---|-----------------|---|---|
| [8 x 12] Ligand Set | $\xrightarrow{\text{Hf}(\text{CH}_2\text{Ph})_4}$ | 1 Hour, Toluene | $\xrightarrow{\text{1) Add Bu}^i_3\text{Al}$<br>$\text{2) Add } [\text{Me}_2\text{PhNH}][\text{B}(\text{C}_6\text{F}_5)_4]$ | Obtain yield, molecular weight, MWD, wt. % 1-octene |
|                     |   |                 | 3) Inject Ligand/ $\text{Hf}(\text{CH}_2\text{Ph})_4$   |   |
|                     |   |                 | 4) Monitor Run for 30 Minutes   |   |

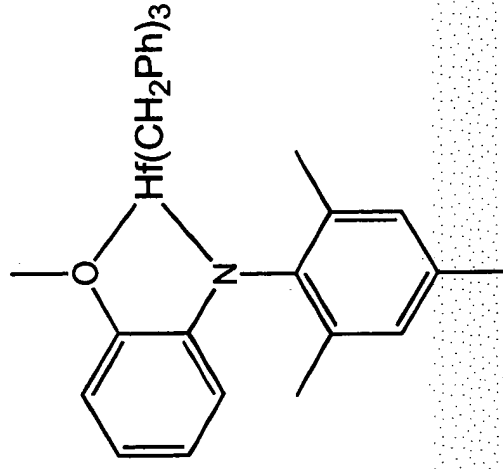
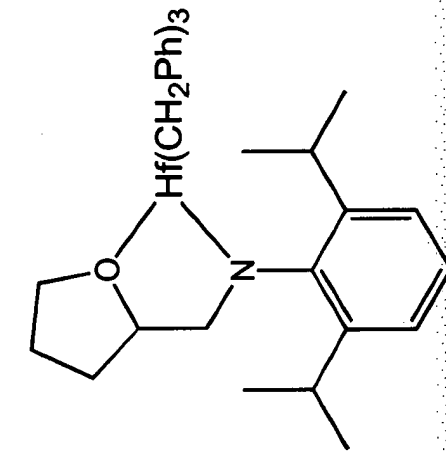
# Focus Library Identifies Large Structure / Activity Effects in this Family, Improved Catalysts





# 1 Gallon Industrial Ethylene 1-Octene Autoclave Results Using Isolated Catalysts Validate Screening Results

Performed in Solution  
Phase  
at 130 °C



Activity (g poly/mmol Hf)	13,760	7,560
$M_w$	181 k	97 k
$M_w/M_n$	2.8	3.0
Density	0.917	0.910

# Conclusions

Effective high-throughput combinatorial methods have been developed for organometallic polyolefin catalyst systems

Months or years of conventional catalyst research can be accomplished in days or weeks

Small-scale 1-octene polymerization screens were validated using a commercial catalyst

New hafnium post-metallocene catalyst family was discovered

Focus library of 96 structural variations was rapidly investigated

- significant enhancements observed
- wide variation in structure / property response

Optimized structures scaled up to commercial-scale process reactors